UNIVERSITY OF PENNSYLVANIA

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CHARLES CLEMENT FRENCH

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY

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THE EFFECT OF NEUTRAL SALTS ON CERTAIN CATALYTIC DECOMPOSITIONS

Introduction

Much experimental material is available on the velocity of reaction of compounds subject to catalytic decomposition by the hydrogen ion and on the effect of neutral salts on such reactions. Similar studies in cases where the catalyst is the hydroxyl ion or another ion are not so numerous. With the idea of contributing more experimental data of a comparatively high degree of accuracy to the field of neutral salt action in homogeneous catalysis, this work has been undertaken.

Two reactions were investigated: 1. The decomposition of hydrogen peroxide, catalyzed by the iodine ion. 2. The decomposition of nitroso-triacetone-amine, catalyzed by the hydroxyl ion, each in the presence of various neutral salts.

It is well known that hydrogen peroxide is completely decomposed by solutions of soluble acid-free iodides, the concentration of the iodide or the iodine ion remaining constant during the reaction. Walton,[1] from a careful study of the velocity of decomposition with sodium, potassium and ammonium iodides, has shown the reaction to be of the first order and complete. He further showed that up to concentrations of the iodides of about $0.04N$, the reaction appears to be proportional to the concentration of the iodine ion, and is independent of the concentration of the water. This then offers one reaction which careful study has shown to be an ionic catalysis, and in which the effect of neutral salts can be studied on an ion other than the hydrogen ion.

Walton has reported only one result on the reaction velocity with each of the following salts: potassium chloride, sodium chloride, potassium sulphate, sodium sulphate, potassium nitrate and potassium chlorate, in a $0.0313N$ potassium iodide solution. The effect of the chlorate was negligible, potassium sulphate decreased the velocity slightly while the other salts increased the velocity.

[1] *Z. physik. Chem.*, 47, 185 (1904).

Harned[2] has studied the effect upon the velocity of this reaction of the addition of potassium chloride, sodium chloride and lithium chloride, up to concentrations of $3N$, in solutions of $0.02N$ and $0.03N$ potassium iodide.

Nitroso-triacetone-amine in the presence of the hydroxyl ion changes into phorone, nitrogen, and water according to the following equation.

$$C_9H_{16}N_2O_2 = C_9H_{14}O + N_2 + H_2O$$

This reaction was discovered by Heintz[3] and has been carefully studied by F. Francis[4] and his co-workers, who showed it to be a simple first order reaction, catalyzed by the hydroxyl ion. At hydroxyl ion concentrations above $0.05N$, the reaction mechanism appears to change since the monomolecular law which holds at lower hydroxyl ion concentrations, fails to hold at these higher catalyst concentrations. More recently this reaction has been investigated by Brönsted and King[5] in connection with secondary kinetic salt effect, and by Kilpatrick[6] in studying catalysis in buffer solutions. Brönsted and King report the effect of sodium chloride in concentrations up to $0.2N$ on the velocity at 15° C., and Kilpatrick the effect of sodium chloride up to about the same concentration on the velocity at various temperatures.

Experimental Methods

Materials.—The action of the following salts was investigated:

1. Chlorides of potassium, sodium, lithium, barium, strontium, calcium and magnesium.
2. Sulphates of potassium, sodium, lithium and magnesium.
3. Bromides of potassium and sodium.
4. Potassium iodide.

All salts were the best grade of analyzed chemicals obtainable. In all cases where there was no fear of decomposition on heating,

[2] *J. Am. Chem. Soc.*, 40, 1461 (1918).
[3] *Ann.*, 187, 250 (1877).
[4] Clibbens and Francis, *J. Chem. Soc.*, 101, 2358 (1912). Francis and Geake, *ibid.*, 103, 1722 (1913). Francis, Geake, and Roche, *ibid.*, 107, 1651 (1915).
[5] *J. Am. Chem. Soc.*, 47, 2523 (1925).
[6] *J. Am. Chem. Soc.*, 48, 2091 (1926).

the salts were ground and dried by careful heating. In several cases, after this treatment further tests were made for water content by heating a weighed sample of the salt at a temperature much above that used in the drying. In no case did the dried salt show an appreciable loss in weight. All salts after drying were tested for neutrality. A sample of the salt was dissolved in about 50 cc. of distilled water and a few drops of indicator added. The addition of a drop of 0.05*N* sodium hydroxide gave a sharp color change in all cases.

The chlorides of lithium, magnesium and calcium were used in solution. The solutions of the first two were made by adding the salts to redistilled water in quantity sufficient to make the solution nearly saturated at room temperature. It was found that this method could not be employed with calcium chloride. Here the analyzed salt was added to redistilled water almost to saturation. The solution was then filtered and a slight excess of hydrochloric acid added to overcome the original alkaline reaction of the solution. Precipitated calcium carbonate was then added in excess to the boiling solution, and the solution filtered while warm. After standing over night the crystals of calcium chloride were filtered, sucked free of mother liquor and dissolved in redistilled water, making the final solution as used. The solutions of the three chlorides were analyzed by taking weighed samples, adding nitric acid and a slight excess of silver nitrate, and weighing the precipitated silver chloride. As a check, the specific gravity of each solution was determined with the Westphal Balance, and the salt content determined from the Tables of Landolt-Börnstein.

The hydrogen peroxide used was a 3 per cent solution. It contained a trace of acid, but as the maximum concentration used was 4 cc. of this solution in 100 cc. total volume of solution, the amount of acid present in the final solution was negligible. That this was true was shown by the fact that neutral potassium iodide liberated but a trace of iodine when added to it.

Nitroso-triacetone-amine as purchased was recrystallized by dissolving in the minimum of alcohol at 50° and precipitating the nitrosamine by the addition of a little warm water. The product thus obtained was pressed dry. It was a pale yellow solid, melting at 72°.

Standard 0.1*N* potassium hydroxide solution was made by diluting a nearly saturated solution of potassium hydroxide, from which the carbonate had been removed by a slight excess of barium hydroxide. While the standard potassium hydroxide solution contained traces of barium hydroxide, the amount present was almost beyond detection, as in the original solution only a trace was present. The water used in making all solutions was redistilled and air-free. The standard alkali solution was kept from contact with the air by a soda-lime tube, and was drawn off through a siphon as used. The solution was analyzed by titration against hydrochloric acid which had been standardized gravimetrically.

Apparatus.—All measurements were made at 25 ±0.01° C. The thermostat was rather large, containing normally about 400 liters of water, and was provided with two large fan-blade stirrers. The heating was controlled by a large grid-shaped thermo-regulator, filled with mercury and having a surface of over 2000 sq. cm. The temperature was controlled with a Beckmann thermometer. Variation in the temperature could not be detected during normal operation for periods of several days or more, and therefore the deviation from 25° during a measurement was probably less than 0.01° C.

The decomposition of hydrogen peroxide is accompanied by the evolution of oxygen and that of nitroso-triacetone-amine by the evolution of nitrogen. Hence the velocity of each of these reactions may be measured by determining either the volume or the pressure of the gas evolved at various time intervals. In working at room temperature, the volume method is more readily applicable, and was adopted. Walton[7] and Francis[8] both obtained sufficient agitation by rapid shaking of the reaction vessel. Brönsted and King[9] also used this method. Harned,[10] and more recently Kilpatrick,[11] used the stirring method for the agitation of the solution. In either case, the important point is "to agitate the solution to such an extent that the gas is registered on the

[7] Ref. 1.
[8] Ref. 4.
[9] Ref. 5.
[10] Ref. 2.
[11] Ref. 6.

volume-measuring apparatus as soon as it is produced in the solution."[12] In this work, the solution was agitated by a rapidly revolving glass stirrer, sealed off from the outside by a mercury seal.

The reaction vessel is shown in Figure 1. *A* is a 500 cc. Pyrex Erlenmeyer flask, in the bottom of which three openings have been made. The tube *B*, sealed in through the first opening, is a 2 mm. capillary through which water or solution was added. The upper end of this tube was connected through a ground-glass slip-on joint to the filling cup *C*. This filling cup was simply the bulb of a 50 cc. separatory funnel, cut off from the tube just below the stopcock. The tube *D*, sealed into the flask through the trap *E*, led to the gas volume burette. The latter was similar to that used by Walton,[13] and contained water. The gas burette was surrounded by a water jacket, maintained at a temperature of 25° by pumping water from the thermostat through it. To the flask at the third opening was sealed the tube *F*, of an inner diameter sufficient to permit the withdrawing of the stirrer. The larger concentric tube *G*, forming a trough for the mercury seal, was sealed to the tube *F*. To the stirrer shaft was sealed the tube *H-H*, of a proper diameter to dip down into the mercury reservoir as shown. The stirrer shaft *J* revolves in two close-fitting brass tubes *K-K*, which in turn are clamped firmly in position. *L* is a pulley which is securely fastened to a piece of glass tubing *M*, which, in turn, is sealed to the stirrer shaft. Since the stirrer was rotated at a high rate of speed, it was necessary that the stirrer shaft be very carefully centered to prevent splashing of the mercury seal and consequent gas leakage.

The following procedure was adopted in making the measurements with the hydrogen peroxide. The reaction vessel was first carefully washed with water and alcohol, and dried in a current of air. The filling cup *C* was then attached at the slip-on ground glass joint, and secured by small rubber bands fastened over the glass hooks at the joint. Then a weighed quantity of salt was added through the tube *F*, or if a salt solution was being used, through the filling cup. Then to this was added the calculated quantity of water, together with 4 cc. of the 3 per cent

[12] Ref. 2.
[13] Ref. 1.

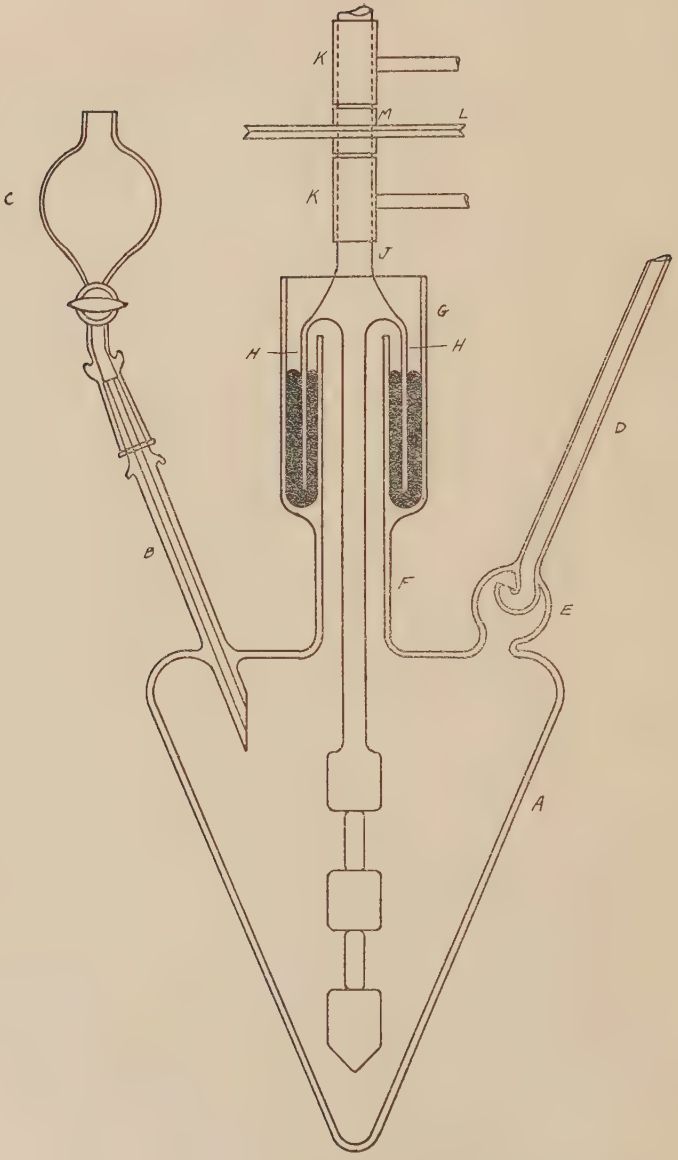

FIG. 1.

hydrogen peroxide solution. The apparatus was placed in the bath and the contents of the vessel stirred until the added salt had dissolved and the solution had come to the temperature of the bath. The stirrer was then removed and the proper quantity of solid potassium iodide, weighed out and wrapped in a small piece of quantitative filter paper, was dropped in. The stirrer was replaced, the gas outlet tube *D* fastened to the gas burette by a piece of tight-fitting rubber tubing and mercury added to make the seal. The stirrer was then rotated and when the potassium iodide had dissolved and a steady evolution of oxygen was assured, readings of the gas burette were begun. Readings were taken at convenient intervals until the decomposition was over 75 per cent complete. After that, in every case, the reaction was allowed to proceed to completion and the final volume recorded.

In the experiments with nitroso-triacetone-amine, essentially the same procedure was followed: 0.15 gr. of the nitrosamine, together with the calculated quantity of water and salt or standard salt solution, were placed in the vessel. The whole was then stirred until solution was obtained and the temperature of the bath had been reached. As the nitrosamine dissolves rather slowly in water at 25°, care had to be taken that sufficient time was allowed for its complete solution. When this was accomplished, the standard alkali solution was added through the filling cup, the delivery tube attached to the gas burette as above and readings begun when about 2 cc. of nitrogen had been evolved. When sufficient readings had been obtained, the stirrer was stopped because of the long time necessary for the completion of the reaction. After standing 24 hours or more, the solution was again stirred for 30 minutes and the final volume then read off the gas burette. Readings of the volume were made to 0.05 cc. In the work with hydrogen peroxide, a total volume of solution of 100 cc. was used: with the nitroso-triacetone-amine, 200 cc.

Effect of Various Salts on the Decomposition of Hydrogen Peroxide, Catalyzed by the Iodine Ion

A number of preliminary experiments were necessary. Hydrogen peroxide solution is slowly decomposed by sharp glass edges and ground glass. In order to determine the extent of this decom-

position, as well as to make sure that the apparatus under the conditions of the experiments was gas-tight, preliminary runs were made with the hydrogen peroxide present in the vessel, but without the catalyst. It was also necessary to determine whether the filter paper, in which the potassium iodide was added, had any effect on the rate of decomposition. Finally, runs were made in the absence of potassium iodide with each of the salts whose effect was to be studied, in order to ascertain whether they alone produced an appreciable evolution of oxygen; and to determine the rate of such evolution if sufficient to make a future correction necessary. These results are summarized in Table I.

TABLE I

DECOMPOSITION IN THE ABSENCE OF POTASSIUM IODIDE

Expt. No.	Substances in Reaction Vessel	Time, hours	Cc. of O_2 Evolved
1	4 cc. H_2O_2 + 96 cc. H_2O	2	0.00
2	4 cc. H_2O_2 + 96 cc. H_2O + filter paper	2	0.00
		3	0.05
3	4 cc. H_2O_2 + filter paper + 96 cc. KBr 3*N*	1	3.3
		2	5.3
		3	8.45
4	4 cc. H_2O_2 + filter paper + 96 cc. NaBr 3*N*	0.5	5.4
		1.5	13.9
		2.0	17.4
5	4 cc. H_2O_2 + filter paper + 96 cc. $CaCl_2$ 1.5*N*	0.5	2.1
		1.0	3.95
		2.0	6.8
6	4 cc. H_2O_2 + filter paper + 96 cc. $BaCl_2$ 1.5*N*	0.5	0.45
		1.0	0.85
		2.5	1.7
7	4 cc. H_2O_2 + filter paper + 96 cc. $SrCl_2$ 1.5*N*	0.75	0.4
		1.5	1.0
		3.0	1.6
8	4 cc. H_2O_2 + filter paper + 96 cc. $MgCl_2$ 1.5*N*	1.0	0.45
		2.0	0.45
9	4 cc. H_2O_2 + filter paper + 96 cc. Na_2SO_4 3*N*	3	0.00
10	4 cc. H_2O_2 + filter paper + 96 cc. K_2SO_4 1.25*N*	3	0.00
11	4 cc. H_2O_2 + filter paper + 96 cc. Li_2SO_4 3*N*	3	0.00
12	4 cc. H_2O_2 + filter paper + 96 cc. $MgSO_4$ 3*N*	3	0.00
A	5 cc. H_2O_2 + 20 cc. KCl 3*N*	2	0.10
		3	0.20
B	5 cc. H_2O_2 + 20 cc. NaCl 3*N* + filter paper	2	0.25
		3	0.40

Experiments A and B in the above table have been taken from Harned[14] and inserted here to emphasize the relation between the various salts used and the magnitude of the effect produced by them in the absence of potassium iodide. The above results show without question that any decomposition due to the apparatus, stirrer or filter paper is negligible. The presence of concentrated solutions of bromides and chlorides does cause a slow decomposition of hydrogen peroxide. Engler and Nasse[15] and Schöne[16] have reported that concentrated chloride and bromide solutions slowly decompose hydrogen peroxide, and that of the two the action of the bromide is the more vigorous. The results reported above confirm this. The magnitude of the corrections will be considered later.

The velocity constants are calculated according to the equation of the first order,

$$K = 2.303/t \log_{10} (V_\infty - V_0)/(V_\infty - V_t)$$

where K is the velocity constant, t the time in minutes, V_∞ the final reading of the gas burette, V_0 the reading at time $t = 0$, and V_t the reading at any time t. In most cases, the calculation of K in this manner gave values of good constancy. In a few cases, the first one or two values of K showed a regular change, and in these cases, the values were discarded and the next reading taken as the new starting point. This recalculation in most cases gave a series of values for K of a satisfactory degree of constancy. If this did not give a series having sufficient constancy, the measurements were repeated with a freshly prepared solution. In Table II, two complete series of constants are given to show the degree of constancy obtainable.

The maximum variation from the mean in the first series is 1.5 per cent, and in the second 1.3 per cent. The maximum variation from the mean in any of the runs giving accepted results was never greater than 2.5 per cent. Duplication of the series with barium chloride, strontium chloride and calcium chloride, as well as repetition of various check points with the other salts

[14] Ref. 2.
[15] *Ann.*, 154, 231 (1870).
[16] *Ann.*, 195, 228 (1879).

showed that the mean value of K could be reproduced in two completely different experiments to within 1.5 per cent. This compares favorably with the constancy and reproducibility reported

TABLE II

VELOCITY OF DECOMPOSITION OF HYDROGEN PEROXIDE SOLUTION

1. Catalyst 0.02N Potassium Iodide. No neutral salt added.

Time, seconds	Gasometer Reading	K
0	7.95	.....
190	11.15	0.0273
555	16.55	0.0271
730	18.95	0.0274
910	21.05	0.0272
1230	24.4	0.0270
1545	27.25	0.0268
2475	33.7	0.0265
3085	36.85	0.0266
	46.7	.....
	Mean K =	0.0270

2. Catalyst 0.02N Potassium Iodide. Presence of N Barium Chloride.

0	10.35	.....
100	13.15	0.0532
270	17.45	0.0538
370	19.5	0.0526
860	27.85	0.0526
1005	29.9	0.0535
1365	33.65	0.0537
1670	36.0	0.0538
2050	38.0	0.0530
	43.4	.....
	Mean K =	0.0532

by Francis[17] and by Walton[18] on measurements of this kind. A further check on the accuracy of the values obtained is found in a comparison of the values for K at a catalyst concentration of 0.02N and in the absence of added salt. While Walton[19] does

[17] Ref. 4.
[18] Ref. 1.
[19] Ref. 1.

not report a result for this exact concentration, the value read for it from a curve drawn through K values for concentrations on both sides of $0.02N$ is 0.0265: Harned[20] reports 0.0275, while the value obtained here is 0.0270. This lies midway between the two other values and differs from each by about 1.8 per cent, which was found to be about the reproducibility in independent experiments.

Referring now to Table I, it is found that the various neutral salts used have rather different effects upon hydrogen peroxide in the absence of potassium iodide. The halides have a rapidly decreasing effect in the order iodide, bromide, chloride, while the sulphates show no action. It is interesting to note that in the case of the chlorides, the magnitude of the effect produced by equivalent salt concentrations is quite different with different cations. Since at 25° these decompositions are quite slow, the value obtained for the infinity reading of the gas burette would have been of very uncertain quality. Hence a number of readings were made over a period of three hours or more (only a few of which are listed in Table I) and from these readings, taking a value for the infinity reading such as to give the greatest constancy to the series of K values calculated, the mean value of K for each decomposition was determined. A summary of these results is contained in Table III.

TABLE III

RATE OF DECOMPOSITION OF HYDROGEN PEROXIDE IN ABSENCE OF POTASSIUM IODIDE

Salt	ΔK per Gram Equivalent of Salt
NaBr	0.0016
KBr	0.0012
$CaCl_2$	0.0013
$BaCl_2$	0.0003
$SrCl_2$	0.0003
$MgCl_2$	0.0001

The corrections to the observed values of the rates of decomposition in the presence of potassium iodide and neutral salts would be less than 1 per cent in the cases of barium chloride,

[20] Ref. 2.

strontium chloride and magnesium chloride, hence no correction has been applied in these cases. With sodium bromide, potassium bromide and calcium chloride the above correction was used. This was taken as proportional to the salt concentration, since it was found that in the pure salt solution the rate was very nearly proportional to the concentration of salt. Table IV contains the mean corrected values of K. All salt concentrations are in weight normality.

TABLE IV

SUMMARY OF RESULTS WITH POTASSIUM IODIDE-SALT SOLUTIONS

Catalyst 0.02N Potassium Iodide. Salt Concentration Varying
Values of $K \times 10^4$

N	NaBr	KBr	$MgSO_4$	Li_2SO_4	K_2SO_4	Na_2SO_4	$MgCl_2$
0.0	270	270	270	270	270	270	270
0.25	...	...	...	...	...	...	297
0.3	...	...	...	...	267	...	...
0.5	292	...	306	296	...	277	348
0.6	...	...	...	...	262*	...	...
0.75	...	...	...	...	...	...	392
0.9	...	...	...	...	259	...	...
1.0	322	293	357	313	...	287	440*
1.25	...	...	...	...	257*	...	491
1.5	356	301.5*	415*	353	...	292*	550
1.75	...	...	...	...	...	...	620
1.8	...	...	...	...	...	289	...
2.0	404	314	491	384*	...	...	706
2.4	...	...	554	...	...	302	...
2.5	452*	332	...	418	...	...	...
3.0	516	344	655	451	...	308	...

N	$CaCl_2$	$CaCl_2$	$SrCl_2$	$SrCl_2$	$BaCl_2$	$BaCl_2 \cdot 2H_2O$
0.0	270	270	270	270	270	270
0.25	333	333	313	...	346	347
0.5	393	387	351	359	402	401
0.75	455	450	422	431	472	459
1.0	529	516	481	491	532	515
1.25	578	579	553	549	604	598
1.5	671	662	643	631	708	...

* Mean of two values.

The graphical representation of these results is shown in Figure 2.

Effect of Various Salts on the Decomposition of Nitroso-triacetone-amine, Catalyzed by the Hydroxyl Ion

Brönsted and King[21] have pointed out that carbon dioxide must be excluded from the apparatus and Kilpatrick[22] worked in an atmosphere of nitrogen, in order to exclude oxygen as well as carbon dioxide, during the course of this reaction. The apparatus as previously described was designed for the hydrogen peroxide reaction, and did not readily permit of operation in an inert gas atmosphere. The purpose of this investigation was not so much to obtain absolute values for the reaction velocity constant as to secure the distribution of the curves caused by the addition of various neutral salts. Recently Åkerlöf[23] has measured the velocity of decomposition of diacetone alcohol to acetone in alkali hydroxide—alkali salt solutions. This work affords one of the few exact investigations of a catalytic decomposition catalyzed by the hydroxyl ion. It was thought that it would be of interest to compare the distribution of the velocity constant curves for a few salts with each of these reactions, since each is a first order reaction catalyzed by the hydroxyl ion. By working at a temperature lower than that used by Francis,[24] and at a much lower concentration of hydroxyl ion, the salt effect would be greater for the same salt concentration and consequently the curves for various salts would be more widely distributed.

The error due to any carbon dioxide in the reaction vessel should also be fairly constant in all experiments, since the same procedure was followed throughout. The alkali solution was never added until just before the vessel was closed off from the air, and the volume of air space above the liquid was always the same. The results seem to indicate that these assumptions were justified, for quite uniform results were obtained, and the curves for the various salts are reasonably smooth.

One other point concerning the measurements should be mentioned. Due to the slowness of this reaction in the presence of salts at fairly high concentrations, the quantity of nitrogen evolved

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[21] Ref. 5.
[22] Ref. 6.
[23] *J. Am. Chem. Soc.*, 48, 3046 (1926).
[24] Ref. 4.

between two readings of the gas burette at ten minute intervals often was not more than 1 cc. An error of 0.05 cc., the limit of accurate reading, would make a much greater variation probable in a series of readings than in the case of the hydrogen peroxide experiments, where from 7 to 8 cc. were collected in the same time. Consequently, for a given series variations of 3 to 4 per cent from the mean value of K were not uncommon. This was also found by Francis,[25] who reported the variation as about 3 per cent, in the volume method of measuring the gas.

TABLE V

SUMMARY OF RESULTS WITH POTASSIUM HYDROXIDE-SALT SOLUTIONS

Catalyst 0.014N KOH. Salt Concentration Varying

Values of $K \times 10^4$

N	KCl	NaCl	LiCl	KBr	KI
0.0	143	143	143	143	143
0.5	120	116	105	107	83
1.0	109	100	84	87	57
1.5	98	...	...	80	46
2.0	93	80	54	65	37
2.5	85	...	...	54	27
3.0	80	57	33	47	23

These results are plotted in Figure 3.

The values for K have been calculated as in the previous work with hydrogen peroxide according to the first order equation, using the minute as the unit of time. While no very good agreement was expected, the value of K for 0.014N potassium hydroxide in the absence of neutral salt was compared with the value of Francis. Since Francis worked at 30°, and did not record a value for K at the concentration of catalyst used here, it was necessary to secure a value from his results comparable with the result found here. From a curve of his values at varying potassium hydroxide concentrations at 30°, the value $K = 0.0250$ at 0.014N was read off. Kilpatrick[26] has recently determined the temperature coefficients of this reaction between 20° and 80°, using sodium hydroxide as the catalyst. He reports $K_{30}/K_{20} =$

[25] Ref. 4.
[26] Ref. 6.

2.57. Assuming that $K_{30}/K_{25} = K_{25}/K_{20}$, K_{30}/K_{25} would equal 1.6. With this value of the temperature coefficient, the value of Francis at 30° becomes 0.0156 at 25°. The value obtained here for the same catalyst concentration is 0.0143, a difference of about 8 per cent, which was a rather unexpectedly close agreement. Table V contains the mean values for K. Salt concentration is expressed in weight normality.

In addition to the experiments with the salts listed above, a considerable number of runs were made with sodium sulphate, potassium sulphate and lithium sulphate. The results obtained were most irregular, in spite of repeated efforts to obtain values which would fall on a smooth curve. In general, sodium sulphate appeared to give a slight increase in velocity; potassium sulphate a decrease, but not approaching the magnitude of that caused by the salts reported above; and lithium sulphate a decrease in velocity approaching in magnitude that caused by sodium chloride. This irregular action with the alkali sulphates agrees with the observations of Francis[27] on the same salts. He also was unable to secure consistent values.

Discussion

In Figure 2, the reaction velocity constant K is plotted against the normal concentration of added salt, the concentration of potassium iodide being kept constant. The results of Harned[28] for the alkali chlorides are plotted with dashed lines. It will be noticed that an increase in velocity is obtained with every salt but potassium sulphate, where there is a slight decrease. Walton,[29] in the single results reported by him for a few salts, obtained a velocity change in the same direction as is here found. Further, the curves are of the same general form as those obtained by Harned for the alkali chlorides. For a given concentration of salt, his curve for sodium chloride is just below the curve for sodium bromide found here, and his curve for potassium chloride just below the potassium bromide curve.

A qualitative similarity between the curves obtained here and

[27] Ref. 4.
[28] Ref. 2.
[29] Ref. 1.

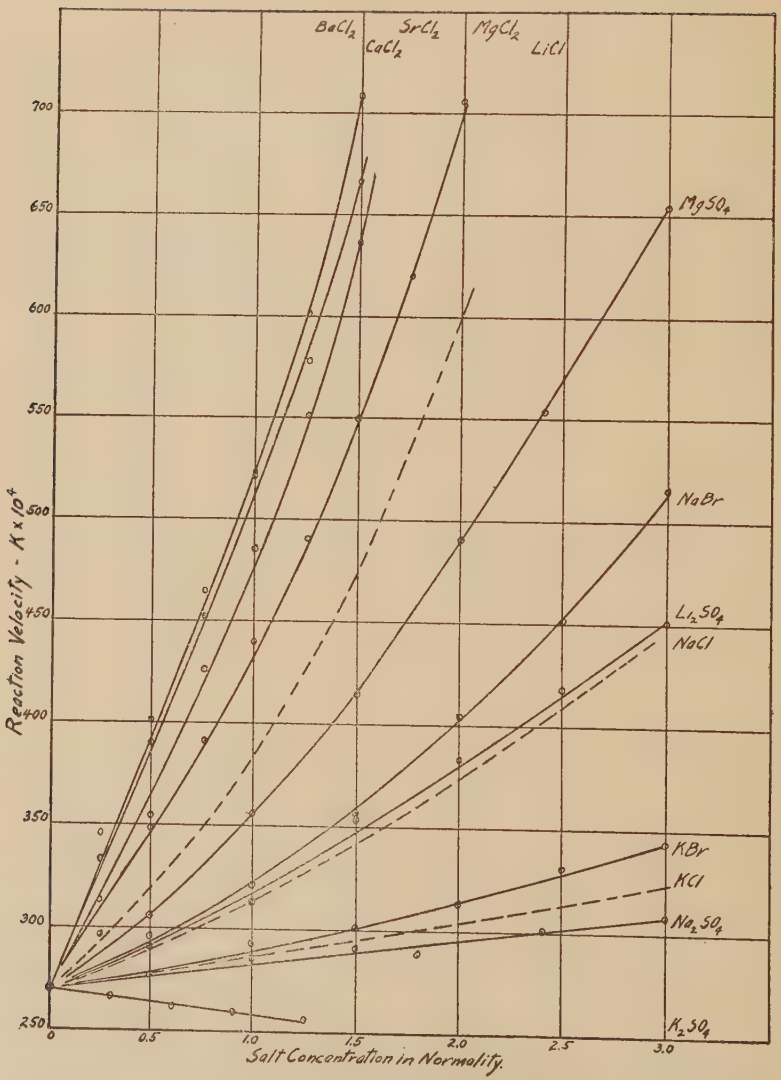

FIG. 2.—Curves for the reaction velocity of the decomposition of hydrogen peroxide in neutral solutions of 0.02*N* potassium iodide and increasing concentration of various salts.

those obtained in a general acid-salt decomposition is of interest. In catalytic reactions of the latter type, the general tendency of neutral salts other than the alkali sulphates is to increase the rate of decomposition, as has been found here. Much recent work has shown that in such reactions, the velocity parallels the activity of the hydrogen ion. From the data compiled by Harned and Åkerlöf,[30] it is seen that the activity coefficient of hydrochloric acid in an acid-salt solution is greater in the presence of lithium chloride than of sodium chloride, and greater in the presence of sodium chloride than of potassium chloride, for the same concentration of salt in each case. From Table III of the same paper, it is seen that the activity coefficients of the alkali chlorides decrease in the same order; lithium chloride, sodium chloride, potassium chloride. From a comparison of the activity coefficients of the alkali earth chlorides, as determined by Lucasse,[31] and the activity coefficients of hydrochloric acid in solutions of the alkali earth chlorides, as determined by Harned and Brumbaugh,[32] it is seen that the same relationship exists here. The activity coefficients of the salts decrease from calcium chloride to barium chloride, and the activity coefficient of hydrochloric acid is greatest in the presence of calcium chloride and least in the presence of barium chloride of the same concentration. From the results of Åkerlöf,[33] it is found that the same relationship holds for sulphuric acid in solutions of sodium, potassium and lithium sulphates. The activity coefficient of the acid is greatest in a solution of lithium sulphate and least in a solution of potassium sulphate of the same concentration. The activity coefficients of the salts follow the same order of decrease. From the above, it is seen that at equal concentrations of salt the activity coefficient of the acid is greatest in that solution where the activity of the salt is the greatest. Hence in acid-salt catalysis, a series of salts such as the alkali chlorides should have an effect increasing in the order potassium-sodium-lithium, if the velocity parallels the activity of the hydrogen ion. Rivett[34] has shown this order to be

[30] *Physik. Zeitschr.*, 27, 411 (1926).
[31] *J. Am. Chem. Soc.*, 47, 743 (1925).
[32] *J. Am. Chem. Soc.*, 44, 2729 (1922).
[33] *J. Am. Chem. Soc.*, 48, 1160 (1926).
[34] *Z. physik. Chem.*, 82, 201 (1913); 85, 113 (1913).

followed in the conversion of acetyl chloraminobenzene to p-chloracetanilide by hydrochloric acid, and Åkerlöf[35] has found the same for the hydrolysis of ethyl acetate by hydrochloric acid in the presence of alkali chlorides.

From Figure 2 it is seen that the alkali chlorides produce an increasing effect on the velocity in the order potassium chloride, potassium bromide, sodium chloride, sodium bromide, lithium chloride. From the values for the activity coefficients of the alkali chlorides mentioned above[36] and those of Harned and Douglas[37] for the alkali bromides, it is found that the activity coefficients increase in the same order. Hence the relation between the activity coefficient of the salt added and the reaction velocity is the same as would be expected in an acid-salt catalysis. While no data are available as to the effect of various neutral salts on the activity of the iodine ion, the marked similarity to the action with the hydrogen ion is rather to be expected. Both ions are of the noble gas type, a simple monatomic ion differing from the atom by only one electron in each case.

The alkali sulphates also show an increasing effect in the order of increasing activity coefficient, potassium-sodium-lithium, a result similar to that in acid-salt catalysis. While the curves are in the expected order, there is one very interesting difference between the two cases. In the hydrogen peroxide catalysis, lithium and sodium sulphates show an increase in the velocity and potassium sulphate only a slight decrease. In acid-salt catalysis, the alkali sulphates produce a decrease in the velocity, and the curves are of an entirely different type than those obtained here. For comparison, we may consider the curves obtained by Åkerlöf[38] showing the effect of magnesium, sodium, potassium and ammonium sulphates on the velocity of hydrolysis of ethyl acetate by sulphuric acid. In each case, the velocity falls very abruptly with the first addition of salt. At a 0.5*N* salt concentration, the velocity of the reaction has fallen to at least 40 per cent of its original value with no sulphate present. Increasing the salt concentration above this value causes only a slight further decrease

[35] *Z. physik. Chem.*, 98, 260 (1921).
[36] Ref. 30.
[37] *J. Am. Chem. Soc.*, 48, 3095 (1926).
[38] *Z. physik. Chem.*, 98, 260 (1921), p. 274.

in velocity, followed by a gradual increase when the concentration of the alkali sulphate increases beyond 1.5*N*. The increase in velocity after the minimum point is passed is most marked in the case of magnesium sulphate. If we turn now to Figure 2, we find no such minimum points with the sulphates. Potassium and sodium sulphates give straight lines, while the lithium and magnesium sulphates curves show a regular rise in the velocity constant with increasing salt concentration. As with the curves for the ethyl acetate hydrolysis, magnesium sulphate shows the most rapidly rising curve with increase in the salt concentration. A possible explanation of this marked difference in the case of the hydrogen ion catalysis and the iodine ion catalysis may be found in the following fact. In the sulphuric acid solution, SO_4 ions and H ions will be in equilibrium with HSO_4 ions. If to the solution there is then added a soluble sulphate, the increase in the concentration of the SO_4 ion will favor the formation of more HSO_4 ions, with the consequent decrease in the H ion concentration of the solution. The effect of this is shown by the abrupt decrease in the velocity of the hydrolysis. In the hydrogen peroxide catalysis with the iodine ion, a similar result would certainly not be expected. Hence the sulphate added shows its effect in a solution in which the catalytic iodine ion concentration remains constant and not as in the acid solution, where the catalytic ion is rapidly reduced in concentration by the added sulphate.

The distribution of curves for the alkali earth chlorides in Figure 2 is not that which would have been predicted. The activity coefficients increase in the order barium chloride-strontium chloride-calcium chloride, and in view of the results obtained with the other salts, it was expected that the order of increasing effect would have been in the order of increasing activity coefficient. When other results were obtained, the entire curves for the three salts were repeated, but no evidence for a re-distribution of the curves resulted. Both sets of results are included in Table IV, and the values plotted are the mean of the two readings for each point. While no cause for this can be given, it is possible that a specific effect of these salts in this particular reaction may counteract the general order of increase with the activity of the added salt.

In Figure 3, the reaction velocity K for the decomposition of nitroso-triacetone-amine has been plotted against the normal concentration of salt added, the concentration of alkali being

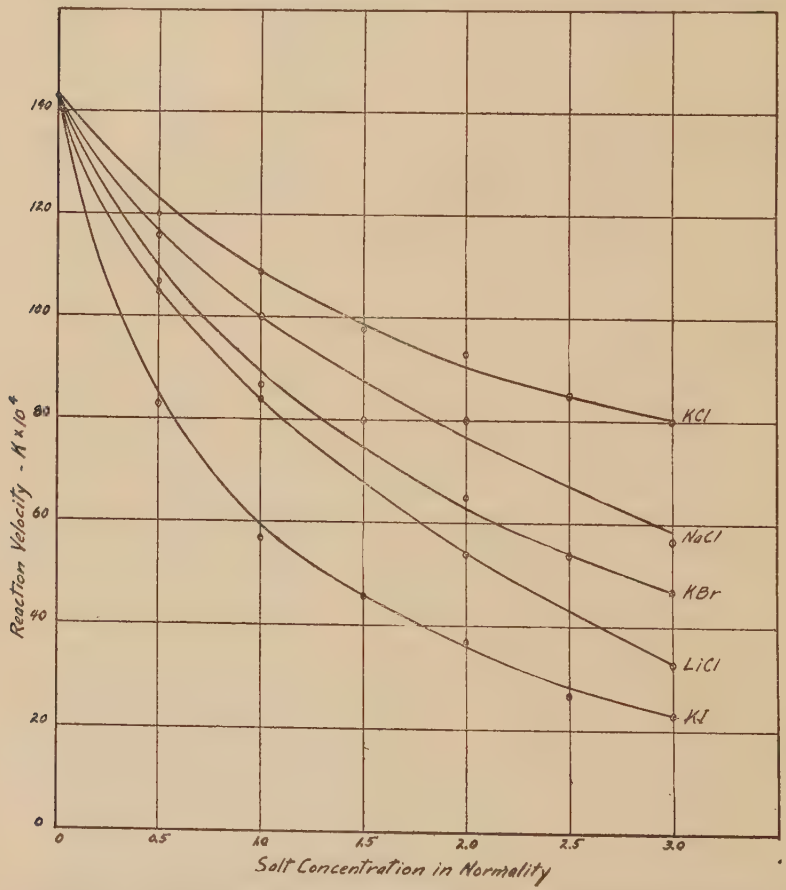

FIG. 3.—Curves for the reaction velocity of the decomposition of nitroso-triacetone-amine in alkaline solutions of different salts at constant potassium hydroxide concentration of 0.014N and increasing salt concentration.

constant. As has been previously pointed out, no great absolute accuracy is claimed for these values, but a very interesting distribution of curves has been obtained. Åkerlöf,[39] in studying the

[39] Ref. 23.

decomposition of diacetone alcohol in alkali hydroxide-alkali salt solutions, has found that the results obtained are always the opposite of those in an acid-salt solution of corresponding concentration. Sodium chloride increases the rate of hydrolysis of ethyl acetate by hydrochloric acid, but decreases the rate of decomposition of diacetone alcohol by a base. He further found that the decrease in decomposition rate was related to the activity of the salt used, the greatest decrease being obtained with the salt of the highest activity. On the basis of measurements of the activity coefficients of sodium and potassium hydroxides in solutions of the alkali halides and sulphates made by Harned,[40] Harned and James,[41] and Åkerlöf,[42] he concludes that the activity of the hydroxyl ion decreases with increasing activity of the salt added. Hence, as in acid-salt solutions, the velocity constant and the activity of the ion acting catalytically follow each other. Here salts would be expected to show a greater decrease in the velocity with increasing activity, because of the coincident decrease in the hydroxyl ion activity. Francis and Geake[43] found a similar behavior in the decomposition of nitroso-triacetone-amine in the presence of the potassium halides, the decrease in velocity being greater in the order potassium chloride-bromide-iodide. This is the order of increasing activity.[44] This result has been confirmed here. Similarly, the effect of the three salts, potassium chloride, sodium chloride, lithium chloride should be to decrease the velocity in the order named, since this is the order of increasing activity.[45] It will be seen from Figure 3 that this result is actually obtained.

Summary

1. The velocity of decomposition of hydrogen peroxide by neutral potassium iodide and of nitroso-triacetone-amine by potassium hydroxide in a number of different salt solutions has been measured at 25° with constant catalyst and varying salt concentrations.

[40] *J. Am. Chem. Soc.*, 47, 676 (1925).
[41] *J. Phys. Chem.*, 30, 1060 (1926).
[42] *J. Am. Chem. Soc.*, 48, 1160 (1926).
[43] Ref. 4.
[44] Ref. 37, p. 3099.
[45] Ref. 30, p. 422.

2. The results in the hydrogen peroxide catalysis gave curves of the general form obtained in acid-salt catalytic reactions. A comparison of the results obtained here showed that in both cases, for the same concentration of salt, the velocity is the greater where the activity of the salt is greater.

3. The results with nitroso-triacetone-amine were found to be similar to those of Åkerlöf on the decomposition of diacetone alcohol in alkali hydroxide-alkali salt solutions. For the same concentration of salt the velocity is least in the case of the salt with the highest activity. In general, the rule seems to hold that in decompositions of the types studied here the rate is directly related to the activity of the ion causing the reaction.